Fig 1 laser

mode

lens

CLIPPEDIMAGE= JP402174123A
PAT-NO: JP402174123A
DOCUMENT-IDENTIFIER: JP 02174123 A
TITLE: FORMATION OF FILM

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INVENTOR-INFORMATION:
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NAME	COUNTRY
NEC CORP	N/A

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INT-CL_(IPC): H01L021/31; C23C016/40 ; H01L021/316
US-CL-CURRENT: 427/583

ABSTRACT:
PURPOSE: To form a gate insulating film by using one kind of film formation
method, whose dielectric breakdown strength is good and which has a good
interface characteristic between itself and a semiconductor layer by a method
wherein a flow-rate ratio of raw material gases is changed while the film is
being formed.

CONSTITUTION: In a silicon oxide film formed between a metal layer and a
semiconductor layer by a photo-assisted CVD method used to form a film by
decomposing a raw-material gas by being irradiated with light, the film of a
part coming into contact with the metal layer is formed under a condition that
a flow-rate ratio of a gas for silicon supply use to a gas for oxygen supply
use is at 1×10<SP>-3</SP> or higher and
1×10<SP>-2</SP> or lower.
In addition, the film of a part coming into contact with the semiconductor
layer is formed under a condition that the flow-rate ratio is smaller than
1×10<SP>-3</SP>. When the flow-rate ratio of the

raw-material gases is
changed, it is possible to obtain an insulating film whose dielectric breakdown
strength is high and whose interface with reference to a semiconductor (silicon
film) is good.

⑲日本国特許庁（JP）　⑪特許出願公開
⑫公開特許公報（A）　平2－174123

⑤1Int. Cl.⁵　識別記号　庁内整理番号　⑬公開　平成2年(1990)7月5日
H 01 L 21/31　B　6810－5F
C 23 C 16/40　　8722－4K
H 01 L 21/316　X　6810－5F
審査請求　未請求　請求項の数　1　（全4頁）

⑤4発明の名称　成膜方法

㉑特　願　昭63－330344
㉒出　願　昭63(1988)12月26日

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⑪出願人　日本電気株式会社　東京都港区芝5丁目33番1号
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明　細　書

1. 発明の名称
成膜方法

2. 特許請求の範囲
光照射によって原料ガスを分解して成膜する光CVDによって金属層と半導体層との間に酸化シリコン膜を形成する方法において、前記酸化シリコン膜のうち前記金属層と接する部分はシリコン供給用ガスの酸素供給用ガスに対する流量比が1×10^{-3}以上1×10^{-2}以下となる条件下で成膜し、前記半導体層と接する部分は前記流量比が1×10^{-3}より小さくなる条件下で成膜することを特徴とした成膜方法。

3. 発明の詳細な説明
〔産業上の利用分野〕
本発明は成膜方法に関するものである。
〔従来の技術〕
TFT（薄膜トランジスタ）等金属電極形成後にゲート絶縁膜を形成するデバイスの場合、ゲート絶縁膜は2つの成膜方法による2層構造がとられている。これは1つの成膜方法による1層の絶縁膜のみでは金属上に発生しがちなピンホールを十分に覆い、且つ半導体層との間に良好な界面状態を形成することが困難だからである。2層構造の例としては半導体層の表面を低温度での光CVDで形成したSiO_2膜で覆い、その後昇温し、大気圧の熱CVDでさらにSiO_2膜を形成するという方法が三村らにより1988年アイトリプルイーデバイスレターズ誌第9巻（ナンバー6）頁290に報告されている。この方法では光CVDから熱CVDへの切換えのため昇温、原料ガスの入替、堆積圧力の設定変更等多くの工程を要する。一方電極形成後その表面を陽極酸化し、その後真空中でゲート絶縁膜、アモルファスシリコンを一貫して形成するという方法が田中らにより1988年テレビジョン学会技術報告頁7に報告されている。この場合、成膜は一貫工程ですむが陽極酸化とい

う基板を水溶液に浸す湿式工程が加わるため工程は簡便化しない。このように従来の方法では1種類の成膜方法で良好な絶縁耐圧を有し、且つ、半導体層との間に良好な界面状態を有するようなゲート絶縁膜を形成することは困難であった。

〔発明が解決しようとする課題〕

本発明の目的はこのような従来方法の問題点を解決し1つの成膜方法のみで、絶縁耐圧が良好で且つ半導体層との間に良好な界面状態を保てるゲート絶縁膜を形成する方法を提供することにある。

〔課題を解決するための手段〕

本発明は上記の従来技術の問題点を解決するために、光照射によって原料ガスを分解して成膜する光CVDによって金属層と半導体層との間に酸化シリコン膜を形成する前記酸化シリコン膜のうち、前記金属と接する部分はシリコン供給用ガスの酸素供給用ガスに対する流量比が1×10^{-3}以上1×10^{-2}以下となる条件下で成膜し、前記半導体層と接する部分は前記流量比が1×10^{-3}より小さくなる条件下で成膜するという手段をとった。

〔作用〕

誘電体はその構成原子の比率によって絶縁耐圧特性、半導体との界面特性などが大きく変化する。この比率は成膜時の原料ガス混合比に強く依存するため、成膜時に原料ガス混合比を変えることによって複数の異なった性質の膜を積層することが一般には可能である。例えばシラン系等のシリコン供給用ガスと、N_2O, O_2 等の酸素供給用のガスとを混合して酸化シリコン膜を形成する場合、シリコン供給用ガスの酸素供給用ガスに対する割合を大きくするとシリコンリッチな膜が形成されることがプラズマ、熱、光等のCVDによる各成膜方法で確認されており、シリコン供給用ガス及び酸素供給用ガスの双方を光化学分解する場合の光CVDでは特にこの現象が顕著になる。これはシリコン供給用ガスが単独で分解した生成物が酸素供給系のガスと反応することなく直接膜中にとり込まれたり、あるいはSi−O−H, Si−O−等の中間生成物の状態で膜中にとり込まれる確率が高くなるためと考えられる。従って化学量論的組成をもつ酸化シリコン膜を形成するにはシリコン供給用ガスの流量に対して酸素供給系ガスの流量を十分に大きくとることが必要である。このようにして得られた化学量論的組成のSiO_2はSiとの間に良好な界面を形成しうる。しかしこの膜の耐圧特性については従来よく知られていなかった。これに関し、シリコン供給用ガスの流量比率が極端に低い成膜系では、得られる膜は良好な界面を形成はするものの緻密さを欠き、絶縁耐圧特性の劣った膜となりやすいことを発明者は実験により見いだした。これは酸素供給用ガス1分子に対し衝突しうるシリコン供給用ガスの分子数が非常に少ないため、成膜初期の核形成密度が低くなる等の理由で粗な膜になり易いためと考えられる。

第2図はシリコン供給用ガスにSi_2H_6を酸素供給用ガスにN_2Oを用いたArFレーザCVDにより得られた酸化シリコン膜の漏れ電流が原料ガス流量比、すなわち(シリコン供給用ガス流量/酸素供給用ガス流量)に依存するという本発明者の実験結果を概念的に示した図である。

領域①は流量比をあげることによってシリコンリッチとなり耐圧が劣化する領域である。これは酸化シリコン膜の抵抗率がシリコンの抵抗率に徐々に近づくために他ならない。一方領域③は流量比を下げることによって化学量論的組成にはなるものの、核形成密度が低いなどのため膜質が粗になりやすく、やはり耐圧が劣化する領域である。

これらの中間にある領域②は、ストイキオメトリックなSiO_2に較べて多少シリコンリッチとなり、Siとの界面準位密度も高めたが、絶縁耐圧にはすぐれた酸化シリコン膜を形成する領域である。

本発明においてはこのように原料ガスの流量比を変えることによって絶縁膜の絶縁耐圧特性、界面特性が変化する発明者が見い出した効果を利用してピンホールが発生しやすい金属膜上は領域②の流量比で、緻密で耐圧特性に優れた膜を、また半導体との界面に接する部分は領域③の流量比でストイキオメトリックで界面特性に優れた膜を、それぞれ成膜する。この複合的な工程によって、

絶縁耐圧が高くしかも半導体（シリコン膜）との界面が良好な絶縁膜が本発明により得られる。さらに、本発明においては、従来方法のように2つ以上の成膜方式を用いる必要がなく、単一装置内で成膜条件を変えるだけで成膜できるので、基板の移し替え作業が不用となるなどコスト削減スループット向上を図ることができる。

〔実施例〕

以下本発明を逆スタガ型のTFTゲート絶縁膜の形成に適用した実施例を図面を参照して詳細に説明する。

第1図は本発明を適用したゲート絶縁膜の形成を行なう装置の模式図である。基板8は排気ポンプのついたCVDチャンバ5に固定し、ArFレーザ1からの出射光をパターンマスク2、合成石英レンズ3、合成石英窓4を通して基板8上にパターン転写する。基板8はガラス上に前工程で形成したクロムのゲート電極を有しており、ヒータ等により適当な温度に加熱されている。原料ガスのSi_2H_6とN_2Oはそれぞれ第1のマスフローコントローラ6、第2のマスフローコントローラ7によってCVDチャンバ5に供給される。堆積開始時にはSi_2H_6のN_2Oに対する流量比が2×10^{-3}以上8×10^{-2}以下になるように第1のマスフローコントローラ6と第2のマスフローコントローラ7を設定する。SiO_2膜厚が2000Å程度になった時点でSi_2H_6のN_2Oに対する流量比が2×10^{-3}より小さくなるように第1のマスフローコントローラ6と第2のマスフローコントローラ7の設定値と変更し、さらに成膜を続け3000Å厚まで成膜を続けた。その後、後工程でa－Si：H層を形成した。

本発明では最初に良好な絶縁耐圧を与える流量比でピンホールが発生しがちな電極付近を覆う膜を形成するので、耐圧不良となることはない。またa－Si：Hと接する部分は良好な組成をもたらす流量比で成膜するので、a－Si：Hとの界面特性も良好に保たれる。

本発明においては原料ガスの流量比を変えるだけで真空一貫で絶縁耐圧、界面特性がともに良好なゲート絶縁膜を形成できるので、基板を1つの装置から他の装置に移す工程が不用であった。

〔発明の効果〕

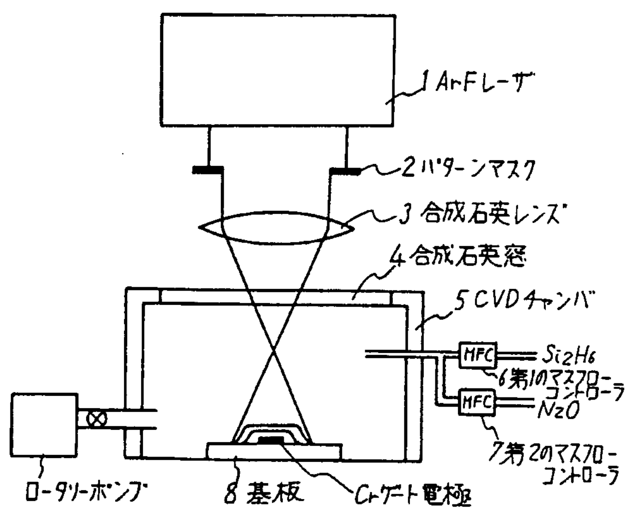
以上説明したように本発明によれば成膜中に原料ガス流量比を変えることによって1種類の成膜方法で、良好な絶縁耐圧を有し、且つ半導体層との間に良好な界面特性を有するゲート絶縁膜を形成することができる。

4. 図面の簡単な説明

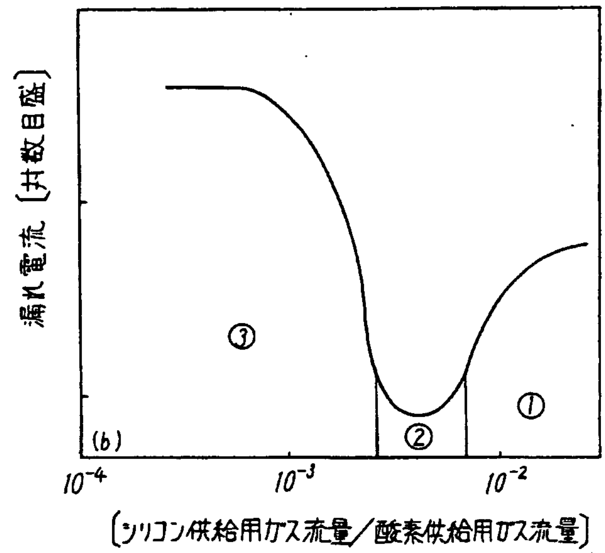
第1図は本発明の方法を適用した装置を表わす模式図、第2図は光CVDで成膜された膜の性質と原料ガス流量比との関係を示す図である。

1……ArFレーザ、2……パターンマスク、3……合成石英レンズ、4……合成石英窓、5……CVDチャンバ、6……第1のマスフローコントローラ、7……第2のマスフローコントローラ、8……基板。

代理人　弁理士　　内　原　　　晋



第 1 図



第 2 図

Jap. doc. et al 9/5/94 (10/3/94)

NEC Corp

* used in rejection

Japanese Patent Laid-Open Number 2-174123

Laid-Open Date: July 5, 1990

Application No.: 63-330344

63 25/88

Application Date: December 26, 1988

Inventor: Toura, Yuko

Applicant: NEC Corporation

original J. pat. doc. missing

IPC: H01L 21/31, C23C 16/40, H01L 21/316

Attorney: Uchihara, Shin

Specification

Title of Invention:

Film formation method

Scope of Claim

A film formation method for forming a silicon oxide film between a metal layer and a semiconductor layer by optical CVD in which a material gas is decomposed by photo irradiation to promote film formation, wherein a portion of said silicon oxide film adjacent to said metal layer is formed under a condition which permits the flow ratio of a silicon supply gas relative to an oxygen supply gas to be 1×10^{-3} or greater and 1×10^{-2} or smaller, and a portion of said silicon oxide film adjacent to said semiconductor layer is formed under a condition which permits said flow ratio to be smaller than 1×10^{-3}.

Detailed Description of the Invention

[Field for Industrial Use]

The present invention relates to a film formation method.

[Background Art]

In a case of a device such as a thin film transistor (TFT) or the like, wherein a gate insulating film is formed after a metal electrode is formed, a two-layered structure is employed for the gate insulating film through use of two types of film formation methods. This is because it is difficult for one layer of an insulating film formed by one type of film formation method to thoroughly cover pin holes that are easily generated on a metal, and at the same time to form a favorable interface state between the semiconductor layer. As one example of the two-layered structure, one is reported by Mimura et al. in IEEE Electronic Device Letters (1988, Vol. 9, No. 6, p.290) which describes a method wherein the surface of a semiconductor layer is covered by an SiO_2 film formed through low temperature optical CVD, and the temperature is then increased to further promote the formation of the SiO^2 film through thermal CVD under atmospheric pressure. In this method, many processes are required, such as temperature increase for switching from the optical CVD to thermal CVD, replacement of the material gas, resetting of the deposition pressure and so forth. On the other hand, Tanaka et al. have reported in "Television Gaku-Zen-Gijustu-Hokoku" (1988, p.7) a method wherein after the formation of an electrode, the

surface thereof is anodized, and thereafter, a gate insulating film, and amorphous silicon are serially formed under vacuum. In this case, the film formation can be conducted in serial processes, however, the method adds the wet process called anodization where the substrate is immersed in a water solution, so that the processes are still not simplified. In this way, it is difficult, with one type of film formation method, to form a gate insulating film with a favorable insulating breakdown voltage and good interface state with a semiconductor layer.

[Problem the Invention Attempts to Solve]

It is an object of the present invention to solve such problem in the prior art, and to provide a method which allows to form a gate insulating film which has a good insulating breakdown voltage, and at the same time, can keep a good interface state with a semiconductor layer, only with a single film formation method.

[Means to Solve the Problem]

The present invention, in order to solve the above problem in the prior art, employs an approach to form said silicon oxide film between the metal layer and the semiconductor layer by optical CVD in which a material gas is decomposed by photo irradiation to promote film formation, wherein a portion of said silicon oxide film adjacent to said metal is formed under a condition allowing the flowing ratio

of a silicon supply gas relative to an oxygen supply gas to be 1 x 10^{-3} or greater and 1 x 10^{-2} or smaller, and a portion adjacent to said semiconductor layer is formed under a condition allowing said flowing ratio to be less than 1 x 10^{-3}.

[Operation]

A dielectric material varies in its insulating breakdown voltage characteristic and interface characteristic with semiconductor depending on the ratio of the constituent atoms thereof. Since this ratio is strongly dependent upon the material gas mixture ratio, it is generally possible to deposit a plurality of films with different characteristics by varying the material gas mixture ratio during the film formation. For example, when a silicon supply gas such as silane type etc. and an oxygen supply gas such as N_2O or O_2 etc. are mixed for the formation of a silicon oxide film, it is demonstrated, in each of the plasma, thermal, optical film formation method etc., that if the proportion of the silicon supply gas relative to the oxygen supply gas is increased, a silicon-rich film is formed, and this phenomenon is particularly significant in optical CVD where the both of the silicon supply gas and oxygen supply gas are photochemically decomposed. This is assumedly because the possibility increases for the products resulted from the solitary decomposition of the silicon supply gas, to be captured directly into the film without reacting with the oxygen supply

gas, or captured as being intermediate products such as Si-O-H, or Si-O etc. Accordingly, in order to form a silicon oxide film having a stoichiometrical composition, the flow of the oxygen supply gas has to be sufficiently large relative to the flow of silicon supply gas. The SiO_2 having a stoichiometrical composition obtained in this manner may be able to form a good interface with Si. However, the issue of the breakdown voltage of this film has not been clearly known in the art. With regard to this issue, the inventor has found through experiments that, with a film formation system having extremely low flow ratio of the silicon supply gas, the resultant film may form a good interface, however it is low in density so that the film is likely to exhibit the inferiority in its insulating breakdown voltage characteristic. It is assumed that since the number of molecules of the silicon supply gas that would collide to one molecule of the oxygen supply gas is extremely small, the nucleation density during the initial period of the film formation becomes low etc. thereby resulting in a coarse film.

Fig. 2 is a graph showing conceptually, the result of the experiment conducted by the present inventor, demonstrating that the leak current of a silicon oxide film obtained through ArF laser CVD using Si_2H_6 for the silicon supply gas and N_2O for the oxygen supply gas, is dependent on the material gas flow ratio (silicon supply gas flow / oxygen supply gas flow). The region (1) is a region in which the film would

become silicon-rich and breakdown voltage would be degraded due to the increased flow ratio. This is exactly because the resistivity of the silicon oxide film is gradually shifting toward the resistivity of silicon. On the other hand, the region (3) is a region which permits the stoichiometric composition due to the reduced flow ratio, however, because of the low nucleation density etc., the film quality tends to become coarse, so that the breakdown voltage is degraded also.

The region (2) between these regions, is a region forming a silicon oxide film which is slightly silicon-richer than the stoichiometric SiO_2, and has a higher interface trap density with Si, however, is superior in the insulating breakdown voltage.

Taking advantage of the effect discovered by the present inventor, in which the insulating breakdown voltage and interface characteristics are varied by changing the flow ratio of the material gasses in the manner described above, the present invention allows to form a film superior in density and breakdown voltage characteristic for the portion on the metal film in which pin holes are easily generated, with the flow ratio in the region (2), and a stoichiometric film superior in the interface characteristic for the portion adjacent to the semiconductor, with the flow ratio of the region (3), respectively. With this composite process, the present invention allows to obtain an insulating film with a high

insulating breakdown voltage and favorable interface with semiconductor (silicon film). Furthermore, the present invention does not require the use of two or more film formation methods as so in the prior art, and since the film may be formed only by changing the film formation condition within a single apparatus, cost reduction and throughput improvement may be achieved (i.e. the relocation of the substrate is not required etc.).

[Embodiment]

The present invention is now explained in detail according to an embodiment with reference to the figure, in which the present invention is implemented in the formation of a reverse stagger-type TFT gate insulating film.

Fig. 1 is a schematic diagram of an apparatus for performing the formation of a gate insulating film according to the present invention. A substrate (8) is fixed in a CVD chamber (5) having a vacuum pump, and a beam emitted from ArF laser (1) is passed through a pattern mask (2), synthesized quartz lens (3) and synthesized quartz window (4) to the substrate (8) for pattern transfer. The substrate (8) has, on a glass, a gate electrode made of chrome which has been formed in a front-end process, and it is heated to an adequate temperature by a heater or the like. The material gasses Si_2H_6 and N_2O are supplied to the CVD chamber (5) respectively by a first mass flow controller (6) and a second mass flow

controller (7). The first and second mass flow controllers (6, 7) are set so that at the beginning of the deposition, the flow ratio of Si_2H_6 relative to N_2O is 2×10^{-3} or greater and 8×10^{-2} or smaller. When the film thickness of the SiO_2 reaches approximately 2000Å, the set values of the first and second mass flow controller (6, 7) are changed so that the flow ratio of Si_2H_6 relative to N_2O becomes smaller than 2×10^{-3}, then the film formation is continued until the film thickness reaches to 3000Å. Thereafter, an a-Si:H layer is formed in a subsequent process.

Since the present invention forms the film initially with a flow ratio which gives a good insulating breakdown voltage for the portion covering the proximity of the electrode, where pin holes are easily generated, voltage breakdown failure would not occur. Furthermore, since the portion to come into contact with the a-Si:H is formed with the flow ratio which gives favorable composition, a good interface characteristic is also kept.

In the present invention, a gate insulating film which is superior in both the insulating breakdown voltage and interface characteristic is formed serially under vacuum by only changing the flow ratio of the material gasses, so that a process to replace the substrate from one apparatus to another is unnecessary.

[Effect]

As explained heretofore, according to the present invention, a gate insulating film having a desirable insulating breakdown voltage and interface characteristic with a semiconductor layer, can be formed through one type of film formation method by changing the flow ratio of material gasses during the film formation.

Brief Description of Figures

Fig. 1 is a schematic diagram of an apparatus in which the present invention is implemented, and Fig. 3 is a graph showing the relationship between the characteristics of the film formed by optical CVD and the flow ratio of the material gasses.

[Description of Reference Numerals]

1: ArF laser, 2: pattern mask, 3: synthesized quartz lens, 4: synthesized quartz window, 5: CVD chamber, 6: first mass flow controller, 7: second mass flow controller, 8: substrate